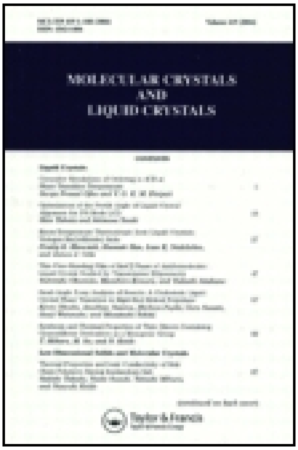

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New Photoactive Organic Semiconductors: Photoconductivity and Schottky Barrier Studies

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NEW PHOTOACTIVE ORGANIC SEMICONDUCTORS: PHOTOCONDUCTIVITY AND SCHOTTKY BARRIER STUDIES*

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The photoconductivity of tetrathia- and tetraselenafulvalenes has been compared with that of squaric acid-based organic dyes, in order to assess their potential for use in photovoltaic systems. Photoconduction action spectra have been measured for single crystals of each compound and compared with photoacoustic spectra. The magnitudes of the dark resistivities and of the photocurrents of these compounds have been compared. The electron-donor compounds are promising candidates for use in photovoltaic systems, so their behavior as thin films was studied. These compounds form potential barriers when sublimed to form films on metal surfaces, although preliminary results indicate that they may not form simple Schottky barriers.

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INTRODUCTION

Interest in photovoltaic energy conversion has grown rapidly in recent years. Since organic semiconductors could offer reduced materials and fabrication costs, studies have been done on various organic photovoltaic systems.[1-8] However, these devices have shown fairly low power conversion efficiencies, because of poor carrier generation and transport properties of the organic materials. In order to better understand the properties of organic semiconductors, we have grown single crystals of two squaric-acid derivatives used in relatively high-efficiency photovoltaic systems,[4,5,7] and studied their dark and photo-conduction. We also hoped to incorporate the improved electron transport properties of the highly-conducting organic complexes into photovoltaic systems, and we have found that some electron-donor compounds are in fact photo-active semiconductors.

RESULTS AND DISCUSSION

Single Crystals

The compounds studied are shown in Figure 1: all are semiconductors, with dark resistivities measured along the

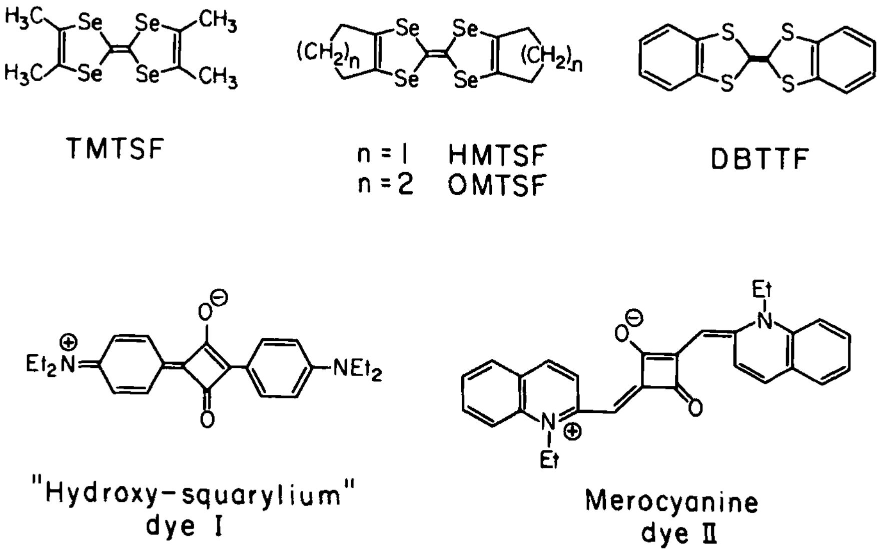

FIGURE 1 Materials investigated.

Table 1 Single Crystal Resistivity Values

Compound		Dark Resistivity (Ω-cm)
TMTSF	unsublimed	7.0×10^7
	sublimed	2.7×10^7
OMTSF	unsublimed	1.2×10^8
	sublimed	3.3×10^7
HMTSF		8×10^2
DBTTF		7.2×10^7
Hydroxy-squarylium I		7×10^7
Merocyanine II		5×10^5
TMTSF[a]	c-axis	8.1×10^7
	b-axis	7.6×10^8
	a-axis	1.3×10^9

[a] All values measured on one crystal

longest crystal axis as listed in Table 1. TMTSF crystals are fairly large parallelpipeds, so the current could be measured along all three crystal axes. The reason for the anomalously low resistivity of HMTSF is not clear.[9]

The photoconduction spectra of TMTSF, OMTSF, HMTSF, and the sulfur-containing analogue DBTTF are compared with their absorption spectra, as measured by photoacoustic spectroscopy, in Figures 2, 5, 6, and 7. All currents were measured along the longest crystal axis; photocurrents along the shorter axes of TMTSF crystals are shown in Figure 3. Sublimation of TMTSF did not affect the spectral characteristics, as shown in Figure 4. Photoconduction and absorption in TMTSF both appear at about 700 nm; although the c-axis photoconduction is low at the PAS peak, the photocurrent along the other two axes is high at this wavelength. The mechanism of the long-wavelength photoconduction in OMTSF is not clear, but this low-energy response is larger in unsublimed samples. HMTSF shows even more pronounced low-energy photoconduction: this peak is so broadened that the photocurrent maximum occurs at 450 nm. DBTTF appears to have a band edge at 570 nm, when both the photoconduction and the absorption rise sharply.

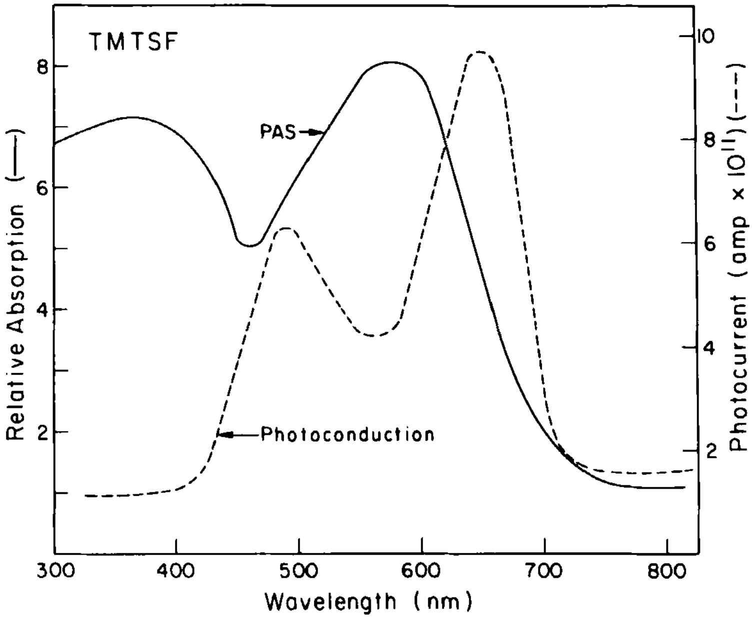

FIGURE 2 Photocurrent and photoacoustic spectra of TMTSF

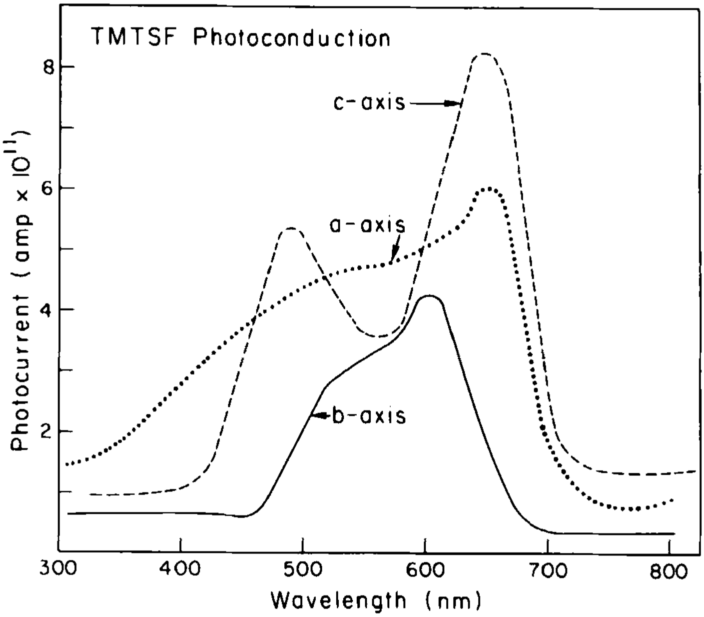

FIGURE 3 Photocurrent spectra along the axes of TMTSF

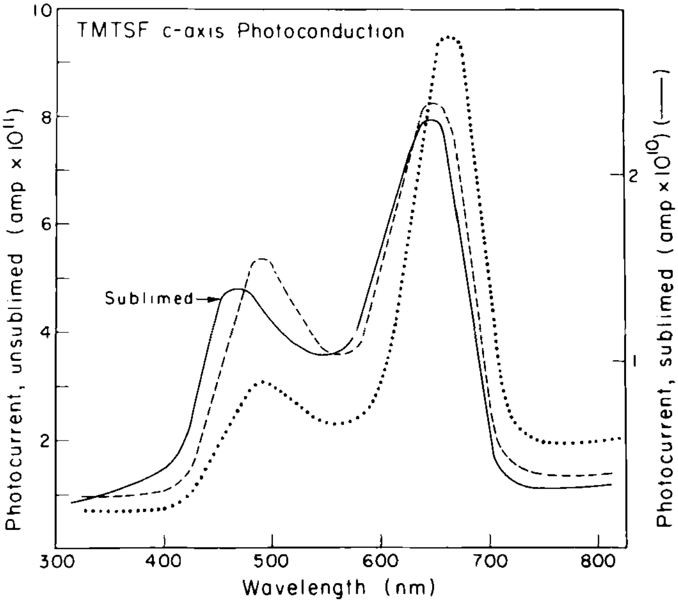

FIGURE 4 c-Axis photocurrent action spectra

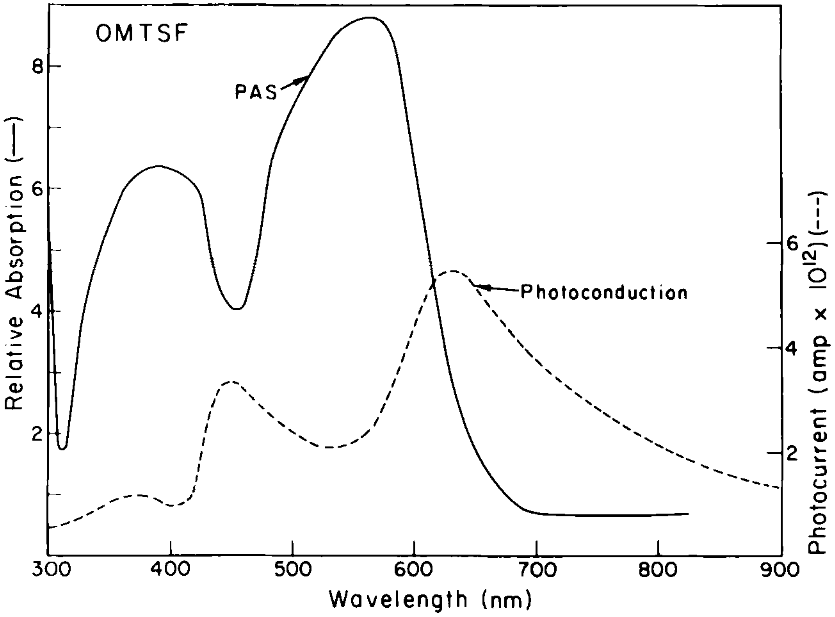

FIGURE 5 Photocurrent and photoacoustic spectra of OMTSF

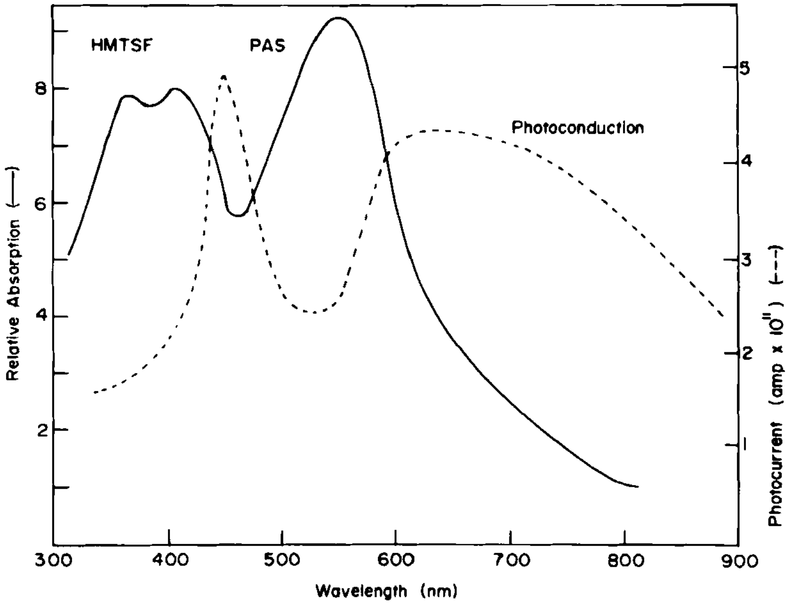

FIGURE 6 Photocurrent and photoacoustic spectra of HMTSF

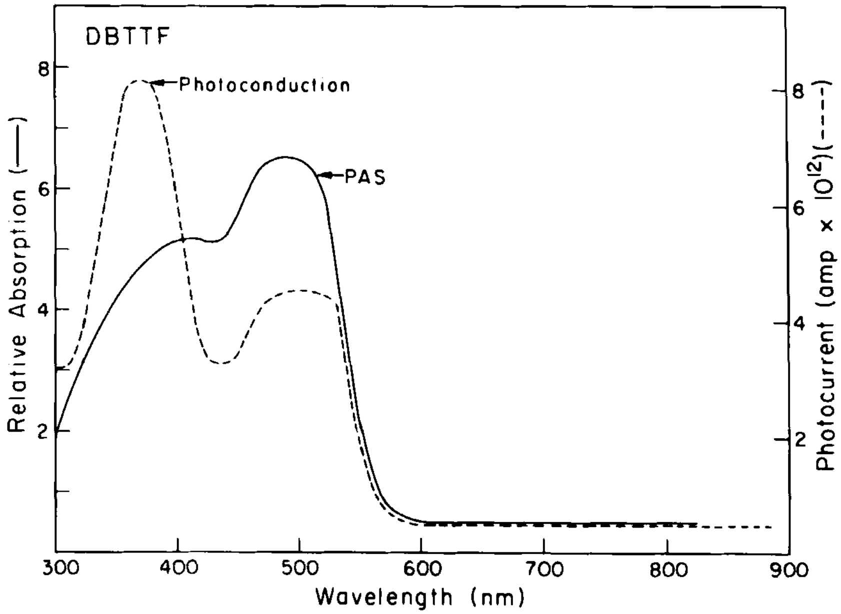

FIGURE 7 Photocurrent and photoacoustic spectra of DBTTF

The photoconduction and absorption spectra of the squaric-acid-derived dyes are compared in Figures 8 and 9. Both dyes show broad responses through the visible region and into the IR, as reported for films of the dyes in photovoltaic devices.[4,5,7]

Photocurrent-to-dark-current ratios were derived from spectroscopic data (Table 2) and were measured for three compounds using a high-intensity mercury lamp (Table 3). The value for HMTSF is again odd, compared to the other electron-donor compounds: apparently the large dark current leaves few carriers to be photo-excited. The dependence of the photocurrent on light intensity for TMTSF and the dyes is distinctly sublinear, but the ratio for TMTSF remains about an order of magnitude higher than that of the dyes. The discrepancy between I_{ph}/I_d ratios for dye I crystals from mesitylene and $CHCl_3$ is not well understood; it may be due to solvent incorporation, or to the fact that crystals from $CHCl_3$ are highly reflective, whereas those from mesitylene are dull blue. Measurements at relatively high light intensities with TMTSF and dye I show that photocurrents for both compounds follow a power law $I_{ph} \propto L^n$, where L is the intensity, with $0.5 \leq n \leq 0.65$.

Table 2 Photocurrent-to-Dark-Current Ratios
($L = 0.12$ mw/cm^3)

Sample	Bias (V)	λ_{max} (nm)	I_d (amp)	I_{ph}/I_d	Rel. I_{ph}/I_d
TMTSF	3	650	4×10^{-9}	5.8×10^{-2}	16
OMTSF	5	675	3×10^{-10}	5.7×10^{-2}	15
HMTSF	1.5	450	4.1×10^{-7}	1.3×10^{-4}	0.035
		610		1.1×10^{-4}	0.030
DBTTF	10	370	4×10^{-10}	2.1×10^{-2}	5.7
Dye I (mesit.)	5	800	3×10^{-10}	1.9×10^{-1}	51
Dye I ($CHCl_3$)	5	830	7.6×10^{-9}	9.2×10^{-3}	2.5
Dye II	5	360	7×10^{-9}	3.7×10^{-3}	1
		825		3.6×10^{-3}	1

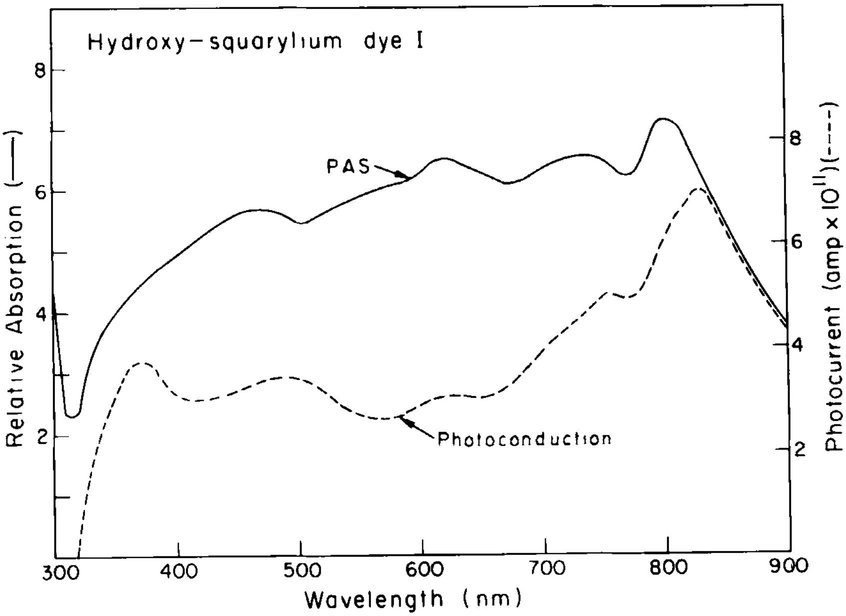

FIGURE 8 Photocurrent and photoacoustic spectra of hydroxy-squarylium dye I

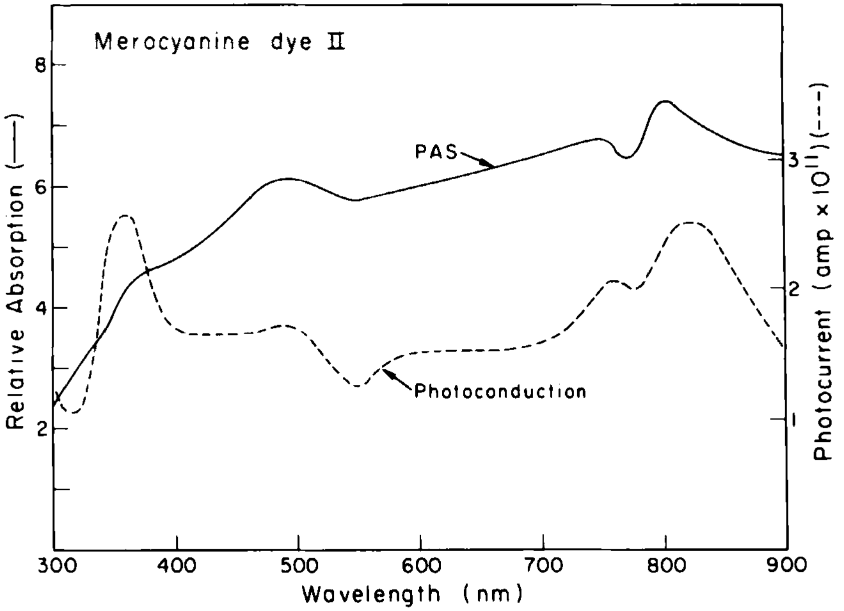

FIGURE 9 Photocurrent and photoacoustic spectra of merocyanine dye II

Table 3 Photocurrent-to-Dark-Current Ratios ($L = 230$ mw/cm^2)

Sample	Hg lines	I_{ph}/I_d	Rel. I_{ph}/I_d	Quantum Effic.
TMTSF	546,577	5.0×10^{-1}	12	5×10^{-6}
Dye I ($CHCl_3$)	"	3.6×10^{-2}	0.9	9×10^{-6}
Dye II	"	4.2×10^{-2}	1	9×10^{-7}

Since the tetraselenafulvalenes photoconduct over a large portion of the visible spectrum, and TMTSF has a larger photocurrent-to-dark-current ratio than the dyes over a wide range of intensities, we were encouraged to try to construct metal-semiconductor potential barriers using these materials. Besides generation of a photocurrent, a built-in potential barrier is the other major phenomenon necessary to obtain a photovoltaic response.

Thin Films

To determine whether these semiconductors form potential barriers at metal interfaces, films of TMTSF and DBTTF have been sublimed onto metal substrates in order to study the current characteristics. The dark I-V curve for such a sample, TMTSF sublimed onto copper with a gallium-indium alloy as the top electrode, is shown in Figure 10. The direction of current rectification indicates an n-type semiconductor forming a barrier at the copper electrode.

If rectification is due to a Schottky barrier, the curve should follow a Shockley-type equation:[10]

$$J = J_o \left[\exp\left(\frac{qV}{nkT}\right) - 1\right]$$

where J is the current density, q the electronic charge, V the applied voltage; k is Boltzmann's constant, T the absolute temperature, and n is an experimental parameter, where n = 1 in the ideal case. Using the thermionic emission model the saturation current density J_o is

$$J_o = \left(\frac{4\pi}{h^3} qm^*k^2\right) T^2 \exp\left(-\frac{q\phi_B}{kT}\right)$$

where h is Planck's constant, m* the effective electron mass (assumed to be 1[6,11]), and ϕ_B is the height of the Schottky

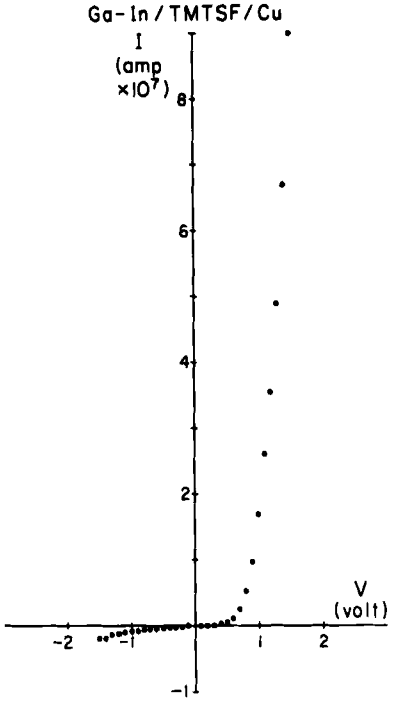

FIGURE 10 Dark current-voltage curve for TMTSF sublimed onto copper, with a Ga-In top electrode (polarity given for copper).

barrier. A plot of log I versus V for the device in Figure 10 is given in Figure 11; the data appear linear at low voltages, although the current saturates at higher levels. However, the slope and intercept of the least-squares line, shown in the figure, give $n = 5.9$ and $\phi_B = 0.90$ V. The very large value of n indicates that these devices do not follow simple Schottky barrier behavior, so the validity of the ϕ_B calculation is in doubt. Similar results were obtained for DBTTF.

EXPERIMENTAL

TMTSF, OMTSF, HMTSF, and DBTTF[12] were purified by column chromatography or recrystallization. One batch of OMTSF (~ 10 mg) was sublimed in a vertical tube at 140°C and 10^{-2} torr; one batch of TMTSF was gradient sublimed, range

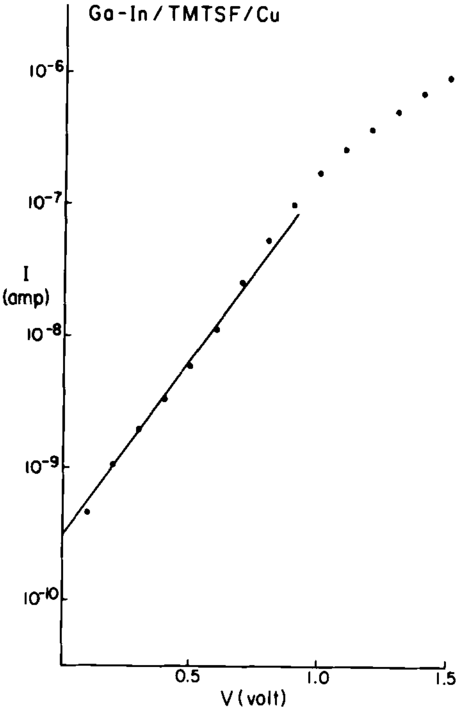

FIGURE 11 Semi-log plot of data in Figure 10.

25°C-150°C, at 2×10^{-2} torr. TMTSF crystals were grown by slow evaporation of CH_2Cl_2 solutions;[13] the sublimed sample was grown under Ar in a dry box. OMTSF crystals were obtained by slow cooling EtOAc solutions, under Ar; HMTSF crystals by slow cooling chlorobenzene solutions; DBTTF crystals[14] by slow cooling a solution in benzene and hexane. Hydroxy-squarylium dye I[15] and merocyanine dye II[16] were recrystallized several times. Dye I crystals were obtained first by slow cooling mesitylene solutions under Ar, then as highly-reflective needles by cooling $CHCl_3$ solutions; dye II crystals by slow cooling DMF solutions under Ar.

TMTSF and DBTTF films were sublimed (130°C, 5×10^{-3} torr) onto copper strips, which had been cleaned with dilute HNO_3. A Ga-In alloy was used as top electrode. Crystals were mounted on IC boards, using silver paste to attach copper and gold leads. Dark I-V curves were obtained with a Keithley 241 High Voltage Supply and a Keithley 602 Electrometer. Photo-measurements, performed at the Applied Physics Laboratory, used a Spex 100-W quartz-halogen light source and Spex Minimate monochromator, with a chopper. The a.c. signals generated were passed through a PAR 173/179 potentiostat to a PAR HR-8 lock-in amplifier. Spectra were recorded on an X-Y recorder driven by the monochromator wavelength drive and the lock-in. Photoacoustic spectra were obtained using a PAS cell built at A.P.L. All spectra were normalized for light source intensity. A high-intensity mercury lamp and neutral density filters were used for intensity-dependence measurements.

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